

REMARKS

Claims 1-4 and 6-14 are pending in this application.

Applicants respectfully traverse the rejections. Applicants further submit herewith an excerpt from Yoshihiro Konishi & Toshiro Tsuji, *Basis and Application of Electroceramics* (1st ed. 1978), along with its English language translation. As this publication is intended only to establish knowledge in the art at the time of the invention, it is not believed that the publication requires the submission of an Information Disclosure Statement (IDS).

For the reasons discussed herein, allowance is earnestly solicited.

Rejections under 35 U.S.C. § 103

Claims 1-4, 6-10, and 12-14 are rejected under 35 U.S.C. § 103(a) as being unpatentable over Kimura et al (US 6093339) in view of Kennedy et al (US 2003/0199228); and

claim 11 is rejected under 35 U.S.C. § 103(a) as being unpatentable over Kimura et al in view of Kennedy et al and Nishida et al (US 2002/0066882).

The Examiner essentially repeats the rejection outlined in the Office Action mailed May 13, 2008. That is, Kimura et al was cited as disclosing a ceramic composition meeting each of the terms of instant claim 1, except for M3, which represents a metallic element of a sintering aid component. The Examiner relied on Kennedy et al as teaching a piezoelectric ceramic composition including M3 which represents a metallic element of a sintering aid component within the claimed amount. The difference is that the Examiner now cites an alternative embodiment of Kimura et al in which $x+y < 0.75$ (see Office Action at col. 3, lines 57-57). According to the Examiner, in this embodiment, the corresponding ranges for a, b, c, d and e would be $0.11025 < a < 0.45$, $0.0441 < b < 0.375$, $0 < c < 0.05$, $0.315 < d < 0.5$ and $0 < e < 0.05$. Therefore,

according to the Examiner, the compositional ranges for a, b, c, d, and e all at least partially overlap the claimed ranges.

The reason for rejection was that it would have been obvious to include a sintering aid M3 of Kennedy et al in the ceramic composition of Kimura et al so as to obtain a ceramic composition that is more easily sintered.

With respect to claim 11, the Examiner concedes that neither Kimura et al nor Kennedy et al expressly discloses that the composition contains the metallic element Sb, wherein Nb in the formula is partially substituted by Bb.

Nishida et al is cited for teaching a piezoelectric ceramic composition in which metallic element Sb partially substitutes for Nb (citing paragraphs 7 and 8).

The reason for the rejection is that it would have been obvious to combine the Sb of Nishida et al with the piezoelectric ceramic composition of Kimura et al as modified by Kennedy et al because Sb is a well-known functional alternative to Nb, and Ta.

Applicants respectfully traverse.

Applicants further submit herewith an excerpt from Yoshihiro Konishi & Toshiro Tsuji, *Basis and Application of Electroceramics* (1st ed. 1978), along with its English language translation.

Instant claim 1, from which all claims variously depend, recites

A piezoelectric ceramic composition characterized by containing:
metallic element K; metallic element Na; metallic element Nb;
M1, which represents a divalent metallic element, or a metallic element combination formally equivalent to a divalent metallic element;
M2, which represents a tetravalent metallic element, or a metallic element combination formally equivalent to a tetravalent metallic element;
M3, which represents a metallic element of a sintering aid component and which is at least one of Fe, Co, Ni, Mg, Zn, and Cu; and

non-metallic element O, wherein, when K, Na, Nb, M1, and M2 constitute the formula $[(1/2)aK_2O-(1/2)bNa_2O-cM1O-(1/2)dNb_2O_5-eM2O_2]$, a, b, c, d, and e in the formula satisfy the following relations: $0.2 \leq a < 0.5$, $0 < b \leq 0.25$, $0 < c < 0.11$, $0.4 < d < 0.56$, $0 < e < 0.12$, $0.4 < a + b + c \leq 0.5$, and $a + b + c + d + e = 1$; and when the total amount of K, Na, Nb, M1, and M2 as reduced to corresponding oxides is 100 parts by mass, the amount of M3 as reduced to M3 oxide is 5 parts by mass or less.

In contrast, Kimura et al nowhere discloses the inclusion of M3, which represents a metallic element of a sintering aid component and which is at least one of Fe, Co, Ni, Mg, Zn, and Cu. As the Office concedes, Kimura et al also fails to disclose that when the total amount of K, Na, Nb, M1 and M2 as reduced to corresponding oxides is 100 parts by mass, the amount of M3 as reduced to M3 oxide is 5 parts by mass or less. See the Office Action: page 3, lines 4-8.

Although the Office Action alleges that Kennedy et al teaches the inclusion of "M3" in its piezoelectric ceramic composition, Kennedy et al actually discloses that less than 2% by mass of a sintering aid comprising Fe_2O_3 , or the like, can be added to a *ceramic composition*. See Kennedy et al at paragraph [0055]. The ceramic composition disclosed in Kennedy et al is used as a wrapping carrier, and not as a piezoelectric ceramic composition. See Kennedy et al's claims and reference numeral (10) in FIG. 2.

Hence, because Kennedy et al is cited for, and merely discloses a known sintering aid for sintering *ceramic material*, the Examiner's conclusion that it would have been obvious to include Kennedy et al's teachings in Kimura et al is inapposite. See the Office Action at pages 7-8, paragraph 20.

It is known in the field of piezoelectric ceramics that piezoelectric characteristics (e.g., piezoelectric strain constant "d33") vary depending on the substance added to the base composition. See attached excerpt from Yoshihiro Konishi & Toshiro Tsuji, *Basis and Application of Electroceramics* (1st ed. 1978). This notion is also evidenced in that Cr_2O_3 ,

Fe₂O₃, CoO and MnO₂ (corresponding to "M3" in the present invention) are described as being added to PZT, thereby impairing piezoelectric characteristics. See id. from page 89, line 1 to page 90, line 7.

In contrast, the present invention aims not at merely improving sinterability, but at improving sinterability without impairing piezoelectric characteristics (e.g., piezoelectric strain constant "d₃₃"). In order to attain this object, the present invention is characterized in that M3 (e.g., Fe, Co or Cu) is added in a specific amount to the base composition as recited in claim 1. The relation between "M3" and the improvement of piezoelectric characteristics is described at paragraph [0014], [0015] of the present PCT specification.

Because it was known at the time of the invention that piezoelectric characteristics vary depending on the added component(s), as described above, Applicants submit that there would have been no motivation to combine references. That is, even if Kennedy et al establishes that Fe, or the like, is added to ceramic (which is generally not a piezoelectric ceramic composition) to merely improve sinterability, those skilled in the art would not have looked to Kennedy to solve the problem of preventing the impairment of piezoelectric characteristics of a piezoelectric ceramic composition. Kennedy et al is unrelated to the technical field of piezoelectric ceramic compositions, and together with Kimura et al, nowhere discloses or suggests all of Applicants' technical findings, or claimed features, which address the relation between sintering aid component(s) and piezoelectric characteristics.

Hence, a skilled artisan would not have found as obvious the features of claim 1, from which all claims variously depend, nor the advantages flowing therefrom, from the description of either Kimura et al and/or Kennedy et al, alone or in combination.

Moreover, Nishida et al is cited for, and discloses only a piezoelectric ceramic composition in which metallic element Sb partially substitutes for Nb. In this respect, Nishida fails to remedy the deficiencies of Kimura et al and/or Kennedy et al.

Withdrawal of the rejection is earnestly solicited.

In view of the above, reconsideration and allowance of this application are now believed to be in order, and such actions are hereby solicited. If any points remain in issue which the Examiner feels may be best resolved through a personal or telephone interview, the Examiner is kindly requested to contact the undersigned at the telephone number listed below.

The USPTO is directed and authorized to charge all required fees, except for the Issue Fee and the Publication Fee, to Deposit Account No. 19-4880. Please also credit any overpayments to said Deposit Account.

Respectfully submitted,

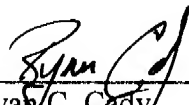
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"Basis and Application of Electroceramics"

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<Page 88, line 8 - Page 89, line 5>

FIG. 4.5 show changes, due to the composition, in the dielectric constant of PbTiO_3 - PbZrO_3 piezoelectric ceramics and the electromechanical binding coefficient. Since this phase boundary hardly changes with respect to the temperature, large piezoelectricity can be utilized stably. PbTiO_3 - PbZrO_3 piezoelectric ceramics has the advantages, for example, that this material has the piezoelectricity approximately twice as high as that of BaTiO_3 and is free of crystalline phase transition within the temperature range of from -50°C to 200°C . By virtue of these advantages, this material has been used later in place of BaTiO_3 , occupying the mainstream of the subject of researches regarding piezoelectric ceramics. However, this material has the disadvantages that PbO evaporates during the sintering process because this material comprises, as main ingredient, Pb in a large amount, causing the difficulty in obtaining a dense sintered body, and that the reproducibility of its characteristics and the uniformity can hardly be ensured due to its dependency, in terms of the piezoelectricity in the vicinity of the phase boundary, on the composition of Ti and Zr . Thus, it has been difficult to put this material into practice.

Then, attempts to improve these disadvantages have been made by a lot of researchers. Examples of the attempts include the method of replacing constituent elements with the same species of elements, as is the case with BaTiO_3 ceramics, or

the method of adding an additive in a minor amount, and researches about the hot-press method. For example, an attempt has been made to replace a part of Pb with Ca, Sr, Ba or Mg. The replacement with an alkali metal in an appropriate amount can increase the dielectric constant without greatly reducing the piezoelectricity.

In addition to the improvement by the replacement of constituent elements, an attempt has been made to improve the disadvantages by the addition of an additive in a minor amount. Almost all oxides have been tried as the additives of this type. Typical oxides, among them, are roughly classified into two groups: "group (I)" La_2O_3 , Nd_2O_3 , Nb_2O_5 , Ta_2O_5 , Sb_2O_3 , Bi_2O_3 , ThO_2 , WO_3 and "group (II)" Cr_2O_3 , Fe_2O_3 , CoO , MnO_2 .

<Page 90, lines 5-12>

On the other hand, the addition of an oxide pertaining to Group (II) generally causes increase in coercive force, resulting in difficulty in polarization so that the piezoelectricity is deteriorated, but increases Q_N and Q_R , thereby forming, what we call, a hard material. Further, the addition of Cr_2O_3 or U_2O_3 provides the effect of decreasing variations in resonance frequency due to the temperature and elapse of time. When these additives are added in small amounts, the additives are considered to uniformly form a solid solution in a composition. On the other hand, the additives, when added in large amounts, prevent the formation of a uniform phase, cause the deposition of a specific compound, and deteriorate the piezoelectricity. For example, when Nb_2O_3 is added in a relatively large amount, Nb is replaced with Zr to deposit ZrO_2 , thereby deteriorating the piezoelectricity. Thus, it is said to be desirable to form a solid solution of $PbNb_2O_6$, when the additive is added in a large amount.

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"Basis and Application of Electroceramics"

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エレクトロセラミックスの基礎と応用

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た。この固溶体系は端成分化合物の PbTiO_3 と PbZrO_3 がそれぞれ強誘電体と反強誘電体であることに興味を持たれ、白根、沢口によって結晶構造との関係が調べられた。図4.4はこの系の状態図と格子定数である。この系は両端成分のほぼ中間組成にある正方晶と菱面体晶の両強誘電相間に相転移境界を有し、この近傍で Ti イオン濃度の増加と共に自発分極の向きは $[111]$ から $[001]$ へ変化し、この過程において結晶構造が不安定となるために誘電的圧電的性質が著しく高められる。

図4.5は PbTiO_3 - PbZrO_3 圧電セラミクスの誘電率と電気機械結合係数の組成による変化である。この相境界は温度に対してほとんど変化しないので、大きな圧電性を安定に利用することができる。その圧電性は BaTiO_3 に比べてほぼ2倍大きく、更に -50°C から 200°C の温度範囲内に結晶相転移がないなどの長所によって、以後 BaTiO_3 に置き換わり、圧電セラミクス研究対象の主流を占めるようになった。しかし、この材料は主成分に Pb を多量含むため焼結過程で PbO が蒸発しち密な焼結体を得にくいこと、また相境界近傍での圧電性が Ti と Zr の組成に依存するために特性の再現性と均一性を保証し難い欠点があり、実用化は困難であった。

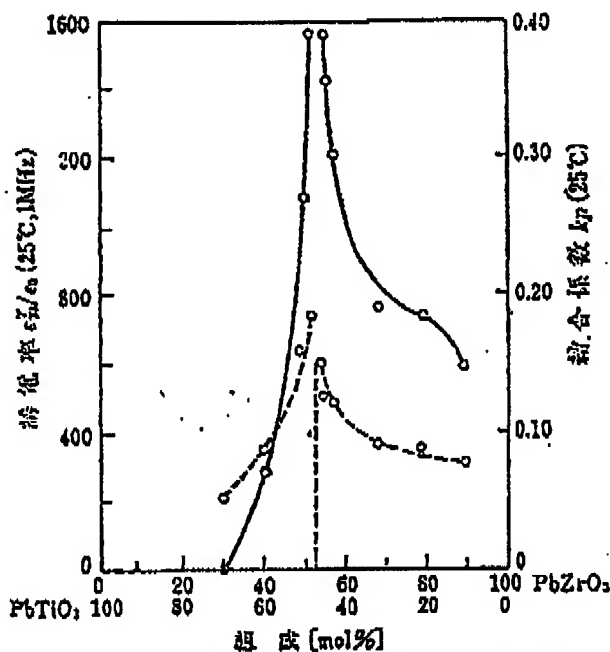


図4.5 PbTiO_3 - PbZrO_3 系セラミクスの誘電率と圧方向結合係数

そこでこれらの欠点を改良する試みが多くの研究者によって行なわれた。すなわち、 BaTiO_3 セラミクスにおけると同様、構成元素を同種の元素で置換する方法、あるいは微量の添加物を加える方法およびホットプレス法に関する研究などである。例えば、Pbの一部を Ca, Sr, Ba, Mg によって置換することが試みられた。アルカリ金属の適量の置換は圧電性をあまり低下させずに誘電率を大きくできる。

構成元素の置換による改良の他に、微量の添加物を加えることによって改良することが試みられた。この種の添加物としては、ほとんどすべての酸化物が試みられている。それらのうちで代表的なものは次の二つの群：(I) La_2O_3 , Nd_2O_3 , Nb_2O_5 , Ta_2O_5 , Sb_2O_3 , Bi_2O_3 , ThO_2 , WO_3 , (II) Cr_2O_3 , Fe_2O_3 , CoO , MnO_2 に大別される。(I)群の添加物は、例えば、 Nb^{5+} は $(\text{Ti}, \text{Zr})^{4+}$ の位置を、 La^{3+} は Pb^{2+} の位置を置換してそれぞれ結晶内に金属イオン空孔を作る。この空孔の形成によって結晶粒内の分域壁の移動が容易になり抗電力が減少すると考えられている。また、 $\text{Pb}(\text{Ti}, \text{Zr})\text{O}_3$ の電気伝導は P 形であるから、 Nb^{5+} のようなドナーの添加

表 4.4 PZT セラミクスの圧電的、誘電的、弾性的特性

	PZT-4	PZT-5	PZT-5H	PZT-6B	PZT-8
結合係数					
k_p	0.58	0.60	0.65	0.25	0.61
k_{31}	0.33	0.34	0.39	0.145	0.30
k_{32}	0.70	0.71	0.75	0.375	0.64
k_{15}	0.71	0.69	0.675	0.377	0.55
圧電定数					
d_{31}	-122×10^{-12}	-171×10^{-12}	-274×10^{-12}	-27×10^{-12}	-97×10^{-12}
d_{32}	285×10^{-12}	374×10^{-12}	593×10^{-12}	71×10^{-12}	225×10^{-12}
d_{33}	495×10^{-12}	584×10^{-12}	741×10^{-12}	130×10^{-12}	330×10^{-12}
g_{31}	-10.6×10^{-3}	-11.4×10^{-3}	-9.1×10^{-3}	-6.6×10^{-3}	-11.0×10^{-3}
g_{32}	24.9×10^{-3}	24.8×10^{-3}	19.7×10^{-3}	17.4×10^{-3}	25.4×10^{-3}
g_{15}	38.0×10^{-3}	38.2×10^{-3}	26.8×10^{-3}	80.9×10^{-3}	28.9×10^{-3}
誘電率					
$\epsilon_{33}^T/\epsilon_0$	1300	1700	3400	460	1000
$\epsilon_{11}^T/\epsilon_0$	1475	1730	3130	475	1290
誘電正接 D	0.40	2.00	2.00	0.90	0.40
弾性定数					
$1/S_{11}^E$	8.2×10^{10}	6.1×10^{10}	6.1×10^{10}	11.1×10^{10}	8.7×10^{10}
$1/S_{22}^E$	6.6×10^{10}	5.3×10^{10}	4.8×10^{10}	10.7×10^{10}	7.4×10^{10}
$1/S_{44}^E$	2.6×10^{10}	2.1×10^{10}	2.3×10^{10}	3.5×10^{10}	3.1×10^{10}
密度 ρ	7.6	7.7	7.5	7.55	7.6
機械的質係数 Q_M	500	75	65	1300	1000
キュリー点 (°C)	325	365	193	~350	300

【単位】 圧電定数 d : m/V, あるいは C/N

誘電正接 D : %

g : Vm/Newton

密度 ρ : 10^3 kg/m^3

弾性定数 $1/S$: Newton/m²

によってP形のキャリアが補償されて抵抗率が $10^2 \sim 10^3$ 倍程度増加する。また、(I)群の添加でセラミクスの分極が容易になるために圧電性が等価的に向上し、分極過程で生ずる内部ひずみを分極後急速に分散させるので経時変化が減少する。しかし、空孔の存在はセラミクス内の弾性波の減衰を大きくし、機械的 Q (Q_M) や電気的 Q (Q_E) の低下をきたし、いわゆるやわらかい材料となる。

一方、(II)群の酸化物の添加は一般に抗電力の増大を招き、従って分極が困難となって圧電性は低下するが、 Q_M , Q_E は大きくなり、いわゆる硬い材料となる。また、 Cr_2O_3 , U_2O_5 の添加は共振周波数の温度および経時変化を少なくする効果がある。これらの添加物の量が少ないとき、添加物は組成中に均一に固溶していると考えられるが、添加量が多いときは均一相にならず、特定の化合物の析出を生じ圧電性は低下する。例えば、 Nb_2O_5 を比較的多量添加すると、NbはZrと置換して ZrO_2 を析出し圧電性を低下するので、添加量の多い時は $PbNb_2O_6$ の形で固溶するのが望ましいといわれている。

添加物を含まない純粋の $Pb(Ti, Zr)O_3$ セラミクスは真性セラミクスと呼ばれ、添加物を加えたものは変性セラミクスと呼ばれている。表4.3には $Pb(Ti, Zr)O_3$ 真性セラミクスの誘電的、圧電的、弾性的諸定数を、表4.4にはClevite (現在Vernitron) 社が開発し市販しているPZT (商品名) セラミクスの諸定数を示す。

4.3.3 三成分系のセラミクス

新しい圧電セラミクスを開発するため $Pb(Ti, Zr)O_3$ の改良と平行して、この二成分に更に ABO_3 の一成分を加えた三成分系の圧電セラミクスの開発が多く研究者によって試みられた。この種で最初に発表されたのは $A^{2+}B^{4+}O_3$ に当る $PbO : SnO_2 - PbTiO_3 - PbZrO_3$ 系である。図4.6はその結晶相図で、正方晶系と菱面体晶系の結晶相境界で誘電性と圧電性が大きく

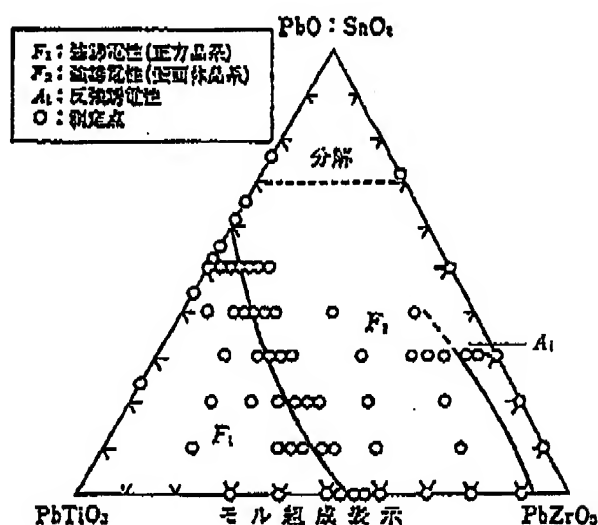


図4.6 $PbO : SnO_2 - PbTiO_3 - PbZrO_3$ 系の状態図 (25°C)

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